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RESEARCH FOR GROUNDWATER QUALITY MANAGEMENT

Clinton W. Hall, Marvin D. Piwoni, and Wayne A. Pettyjohn

> "The fact that a problem will certainly take a long time to solve, and that it will demand the attention of many minds for several generations, is no justification for postponing the study." T. S. Eliot [1]

INTRODUCTION

Groundwater is a valuable resource because of both quality and availability. It is available in most locations in quantities large enough to provide for domestic needs; 50 percent of the population of the United States is dependent on groundwater.[2] In fact, groundwater supplies about 25 percent of all the fresh water used in the United States. This Country's fresh groundwater supply, within one-half mile of the earth's surface, constitutes about 150 trillion cubic meters or roughly 4 times the volume of the Great Lakes.[3] Groundwater recharge occurs at a rate of about 1 trillion cubic meters per year, implying that something approaching 150 years would be required to flush the system once, assuming that the recharge rate applied equally to all aquifers. Groundwater is a reliable resource not subject to extremes in

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Clinton W. Hall, Director, Robert S. Kerr Environmental Research Laboratory, OEPER, ORD, Environmental Protection Agency, P. O. Box 1198, Ada, Oklahoma 74820

Marvin D. Piwoni, Physical Scientist, Robert S. Kerr Environmental Research Laboratory, OEPER, ORD, Environmental Protection Agency, P. O. Box 1198, Ada, Oklahoma 74820

Wayne A. Pettyjohn, Professor and Head, Department of Geology, Oklahoma State University, Stillwater, Oklahoma 74078

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16. ABSTRACT

Ground water is an excellent resource due to its quality and availability. In the United States it is available at almost any location in quantities large enough to provide for domestic needs and over one-third of the Country is underlain by aquifers capable of yielding 100,000 gallons or more daily on a sustained basis. This expansive nature of ground water is paradoxical in terms of its ability to meet water supply requirements over long periods of time. It is subject to contamination from a host of sources and is probably the least understood of all our major natural resources. A ground-water research strategy is presented which divides research consderations into three areas based on the types of processes that will effect pollutant movement in the subsurface: (1) hydrologic; (2) abiotic; and (3) biotic processes. Research under each of these process areas is further organized into a framework of research elements focusing on methods development, subsurface characterization, pollutant attenuation, process kinetics, field application, and mathematical model development and application. Each of these research elements represents a series of tasks or specific questions that need to be addressed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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temperature or quality fluctuations, and it is buffered from the floods and droughts, which affect surface supplies. The development of subsurface water supplies has little effect on land use and can usually be accomplished at relatively low costs compared to development of surface supplies.

This expansive nature of groundwater is paradoxical in terms of its ability to meet water supply requirements over long periods of time. On the one hand, groundwater is available in various quantities nearly everywhere; on the other hand it is subject to contamination from a host of sources. Despite the remarkably accurate observations of da Vinci in the 15th century, John Ray and Descartes in the 17th century, Henry Darcy in the middle 19th century and the continual scientific accomplishments since that time, groundwater remains probably the least understood of all our major natural resources. Courts of law have erroneously described it as "underground streams" and the general public often thinks of it as a large underground "reservoir" similar to surface impoundments.

The subsurface environment is a complex system subject to extensive physical, chemical, and biological variations within small vertical or horizontal distances. This complexity is profoundly accentuated on a macro scale in terms of the multiplicity of materials comprising aquifer and soil systems. Clays, sands, silts, loams, and the various rocks and organic residues which constitute the subsurface matrix each play a unique role in water supply and waste disposal systems.

The extremely slow movement of pollutants through the subsurface environment is generally not appreciated. The residence time of many pollutants in groundwater can be measured in centuries as compared to days to years for surface water.[3] The soluble nitrate ion may take 8 to 50 years to move only 30 feet in saturated alluvial materials while the movement of metals and some organic compounds and their degradation products may occur at even slower rates. One result is that the hydrodynamic forces acting in the subsurface produce little dilution of chemical contaminants.[2]

Because of the protracted effects of contamination and problems of accessibility, the restoration of underground water quality is difficult and expensive with costs generally exceeding the short-term value of the resource as compared to the costs of alternatives. For this reason, it is widely agreed that the most viable approach to groundwater quality protection is one of prevention rather than cure.

An understanding of the processes that effect the movement and degradation of contaminants in the subsurface is essential for effective groundwater quality management. The state of knowledge concerning these processes is, in many ways, insufficient to ensure protection of groundwater quality without excessive restrictions on other surface and subsurface activities. The purpose of this chapter is to provide an organized approach to acquiring the knowledge necessary for effective and efficient groundwater quality management.

GROUNDWATER CONTAMINATION

Contamination of groundwater from human activities may come from numerous sources and activities including: surface impoundments, landfills, agriculture, leaks and spills, land disposal of wastes, septic tanks, mining, petroleum and gas production and storage, underground injection of wastes, and other miscellaneous activities. The disposal of industrial wastes in impoundments and at solid waste disposal sites is considered the most important source of groundwater contamination from a public health consideration.[4] It is estimated that approximately 15 percent of the liquid and solid industrial wastes generated in the United States can be classified as hazardous. There are about 35 million tons of hazardous wastes produced annually in this country by 270,000 generators.[5] Although concentrations of toxic material from other sources are lower than from industrial wastes, they can be very significant on a regional basis where large amounts of groundwater may be degraded from numerous low level sources. It can be concluded that in an area of substantial manufacturing activities and large numbers of people, there exists the potential for pollution of the groundwater resource. The same conclusion can be drawn for areas where mining, agriculture or petroleum production are the major activity.

An extended period of time is usually required for movement of a pollutant from the land surface through the soil profile

to underlying groundwater. The overland movement of pollutants from a source to a stream or lake may require only hours or at the most a few days, but in the subsurface the movement to the groundwater may take weeks or, in some cases, even years. This transport time is dependent on many variables including rainfall occurrence, intensity and duration, subsurface physical properties that control percolation rates and the nature of interactions between the pollutant and the subsurface materials. Thus, activities that involve introduction of chemicals to the land surface may continue for many years before the pollutants are detected in the groundwater. In fact, in some cases, the pollutant sources may be gone and forgotten before the groundwater problems become apparent.

The length of time required for this vertical movement makes problem identification and correction very difficult, if not impossible, if monitoring is limited to the groundwater only and not to the activities that might cause the problem. Given the slow movement of groundwater and the attenuated transport of many pollutants it becomes very clear why it is difficult to monitor and study groundwater contamination problems within the aquifer.

The threat to groundwater by man's activities on the surface depends on several factors but local geologic and hydrologic conditions are major influences. For example, a dump located on top of a thick continuous layer of low permeability clay

poses little danger to the underlying aquifer when compared to the same dump placed on highly permeable material such as sand and gravel (assuming no lateral discontinuities in the clay layer). The concentration, size and shape of a contaminant plume in groundwater is dependent upon the nature of the contaminant and the water bearing properties of the aquifer. Even though moving slowly, pollutants can, with time, move great distances and because of the nature of groundwater flow be present in high concentrations in one well, but not present in a well only a short distance away.

While the existence of our groundwater contamination problems can not be denied, the very nature of the groundwater environment and the extremely slow rate of movement of groundwater tend to limit the spread of pollutants in the subsurface and ameliorate the severity of the problem. Although evidence of groundwater contamination is found in many places, the volume of groundwater contaminated is small compared to the enormity of the resource. Aquifers already contaminated may, however, remain so for a long period because practical technology for purifying them has only recently been under development.

There will always be alternative management practices for obtaining water of adequate quality from subsurface supplies. One may treat only that water withdrawn from the aquifer before use, protect the aquifer totally from all

possible contaminant sources, or reclaim an aquifer after it has been contaminated. The first option has traditionally been selected for surface water supplies as it works very well for common problems such as sediment and low levels of most bacteria. Now we are finding that chlorination can produce trihalomethanes and this problem can extend to groundwater supplies as well. In addition, since most pollutants reaching groundwater are not readily filterable it becomes obvious the first option can become very expensive if groundwater is allowed to become contaminated.

The second option has worked well for streams and for some man-made lakes. For groundwater, this approach would require land use control to protect recharge zones--a generally unpopular strategy when imposed by federal or state governments. Best management practices, such as more efficient and better timed fertilizer and pesticide application, may be the most palatable approach to the public but may not be sufficiently effective in sensitive areas. Man has encountered serious problems trying to restore natural lakes because of the time required for nature to act on water that is not flowing. The uncertainties of the purification processes at work in the subsurface do not allow prediction of natural restoration time for contaminated aquifers. The problem may take hundreds or thousands of years to correct naturally in the groundwater environment.[6,7]

The third option assumes that man can restore the quality of the water in a water resource. This has been tried with various degrees of success in this Country with lakes and has proven very expensive. The process of cleaning or restoring a portion of an aquifer presents many more problems than encountered in lakes and would, therefore, be more costly, although in some cases, it may be the only alternative.

LEGISLATIVE BASIS FOR GROUNDWATER QUALITY MANAGEMENT

In times of shortages, we hear the cry that we are "running out of water." This, of course, is not the case since the world's total water supply is not diminished. The continents are not running out of water, but the time is getting short to stem waste of fresh water and the destructive exploitation of the environment before the harm done becomes irreparable.[8] Despite outcries of water shortages, a principal use of water in advanced civilizations and industrialized nations is for waste disposal practices. A major problem in most parts of the world is a shortage of water development and management facilities, not a shortage of water.

It was not until the middle of the last decade that water resource experts and legislative bodies began to pay proper attention to our underground water resources. This attention undoubtedly resulted from a number of causes including severe droughts, particularly in the western states, and reports of toxic organic chemicals in the northeastern states. Advances

in analytical techniques during this time allowed for pollutant measurements not possible earlier, making it apparent that past waste disposal practices were degrading groundwater quality throughout much of the Country.

Federal authority to address groundwater quality problems is embodied in at least eight statutes dealing primarily with surface water.

An effective groundwater quality management strategy must be flexible. Groundwater resources throughout the nation vary in quality, quantity, hydrologic characteristics, use and economic value. No single, rigid approach can work well in all places. The division of authority and responsibility between state and federal governments relating to control of groundwater resources must allow for this flexibility.

The Rivers and Harbor Act of 1899 was aimed at preventing waste discharges that resulted in obstructions to navigation. This Act is still in effect and did serve as the basis for permits for waste discharges administered by the Corps of Engineers and the Environmental Protection Agency (EPA) until passage of Public Law 92-500. This legislation has been used against landfill operators because of leachate being discharged to navigable waters.

The Water Pollution Control Act of 1956 was amended over the years, evolving into the Federal Water Pollution Control Act (PL 92-500) in 1972 and the Clean Water Act in 1977. The law addresses the Nation's groundwater in several sections either

directly or by implication. Section 102, in which groundwater is specifically mentioned, deals with the preparation of comprehensive programs for preventing, reducing, or eliminating pollution of navigable waters and groundwater and improving the sanitary condition of surface and underground waters. Groundwater is also mentioned in Section 104, entitled "Research, Investigations, Training, and Information," which provides one authority for federal funding of groundwater quality research. Although groundwater is not specifically mentioned in Section 208, it still provides a potentially effective tool for quality protection in calling for state areawide planning in pollution control giving consideration to nonpoint sources of pollution. Section 304 mentions groundwater in calling for information on the presence of pollution and processes, procedures, and methods by which it can be controlled. While the Water Pollution Control Act contains many provisions relating to groundwater, it is aimed primarily at pollution control of navigable waters with its eventual goal being the elimination of waste discharges to these waters. Ironically, this philosophy may result in increased stresses on groundwater resources because those wastes previously discharged to streams and rivers will instead be applied to the land or injected underground.[9]

The National Environmental Policy Act implemented in 1970 did not create a regulatory vehicle but did require that federal agencies consider the environmental consequences of their actions. Under the Act, Environmental Impact Statements must be prepared

for projects that might have a significant adverse effect on surface or groundwater quality or quantity.

The Safe Drinking Water Act became law December 16, 1974. It provides for safe drinking water for all Americans served by public water systems and, in doing so, adds a large dimension to the protection of groundwater. In addition to establishing minimum drinking water standards, regardless of the source, it addresses the protection of groundwater quality and provides for research, technical assistance, and personnel training. The Act, however, does not provide protection for the millions of rural Americans on private wells. Section 1424(e) allows EPA to determine that an aquifer is a sole or principal source of drinking water. If such a determination is made, no project requiring federal assistance may be initiated that may contaminate the aquifer through a recharge zone and result in a significant hazard to public health.

Both the Toxic Substances Control Act (PL 94-469) and the Resource Conservation and Recovery Act (PL 94-580) were enacted in October 1976. The first makes no direct reference to groundwater but is intended to protect the environment, which includes "...water, air, and land, and the interrelationship which exists among and between water, air, and land of all living things." The Resource Conservation and Recovery Act requires the establishment of guidelines for solid waste management. It further requires that these guidelines provide for the protection of the quality of groundwaters and surface waters from leachates. It is significant

that the term solid waste is defined to include solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations, and from community activities.

The Surface Mining Control and Reclamation Act of 1977 empowers the Department of Interior to issue operating permits, and to require mining and reclamation plans, and reclamation bonds. It also has provisions aimed at the prevention of chemical contamination and hydrological disruption of groundwater.

In 1980, Congress enacted the Comprehensive Environmental Response, Compensation, and Liability Act which authorizes government responses to spills of hazardous substances as well as clean-up of abandoned hazardous waste sites. The Act defines "environment" to include groundwater and establishes a $1.6 billion fund for cleaning up hazardous waste sites.

State jurisdiction over groundwater quality, like the federal situation, has generally taken a low priority due to competition with surface water. This is further complicated by the complexities and diversity of ownership from one part of the Country to another.

The protection of groundwater quality in most states is gained from statutes dealing with surface water which generally are based on public health.[9] Land-use regulations are also used to protect groundwater quality by locating waste sources, such as lagoons and solid waste facilities, in areas to minimize the pollution potential.

Construction regulations are often used in a secondary manner to protect groundwater. For example, water wells are constructed primarily to prevent contamination of the well with little thought given to protecting the area's groundwater. Septic tank regulations are aimed specifically at controlling surface discharges, disease, and nuisance in much the same way as landfills are designed to prevent smoke, odors, rodents, and unsightliness.

It is significant to note that most litigation concerning groundwater pollution is decided on the basis of trespass, negligence, or nuisance rather than violations of state statutes and almost every case of groundwater contamination is discovered only after drinking water has been affected.[9]

The most promising management option now available is to protect the groundwater resource from contamination. This will require many different "best management practices" for use by man as he seeks to control those activities that threaten the resource. It will require an understanding of the many processes that are involved in pollutant transport and transformation, both in the unsaturated zone and within the saturated groundwater environment.

One simple solution would be to ban, from the recharge zone, all land use practices that could contribute pollutants to the aquifer. While this might work in some instances it simply cannot be adopted totally in any practical way. The community of man will continue to produce waste products as a result of

those activities deemed necessary to support a contemporary standard of living, and those wastes must be managed with considerable thought given to economics.

Some wastes, due to their high inherent toxicity, should probably not be disposed of on the land. For these, incineration or eternal encapsulation offer the principal management technologies. For other less hazardous chemicals nature itself can provide economical treatment alternatives to render them environmentally acceptable. The key is to understand the natural abiotic and biotic processes, which are known to function in the subsurface environment, so that we can manage our wastes in such a way as to provide maximum protection to groundwater while allowing the continuation of selected land use activities.

RESEARCH NEEDS

The technical information requirements for development of a viable groundwater management scheme have been identified and refined over the last few years through the involvement of the United States Environmental Protection Agency (EPA), the National Drinking Water Council, the Subcommittees on the Environment and Atmosphere of the House Subcommittee on Science and Technology, the EPA's Science Advisory Board, as well as universities, private consultants, state and federal agencies, and the National Water Well Association. These requirements have been partitioned into seven groundwater research categories: 1) methods development; 2) contaminant transport and fate; 3) subsurface characterization; 4) specific sources of contamination; 5) aquifer rehabilitation;

6) information transfer; and 7) technical assistance. Two additional research areas, health effects and water treatment, extend beyond the purview of strictly groundwater concerns.

The first three categories of research are fundamental to understanding the processes that function in controlling the behavior of pollutants in the subsurface. These categories, which form the basis of the strategy for groundwater research developed in this chapter, are discussed in some additional detail below.

Methods Development

Methods development includes the improvement of any technology which can be utilized to conduct groundwater investigations. For example, there is a need for noncontaminating well drilling techniques, pumps designed to allow for uncontaminated sampling of trace organic substances in groundwater, methods for detecting and quantifying biological activity (which may indicate pollution and/or breakdown contaminants), and methods for locating abandoned injection wells and other possible sources of contamination such as cisterns, abandoned dump sites, and domestic and oil/gas wells. Further, there are needs to develop methods for laboratory evaluation of pollutant behavior in the subsurface, and to define techniques that allow application of laboratory data to the environment.

The inaccessibility of an undisturbed subsurface environment hinders the identification of appropriate sampling locations and adds an atmosphere of unpredictability to and significantly increases the cost of obtaining representative data. Additionally,

the options available for the determination of groundwater quality, the reclamation of groundwater, and the measurement of predicted pollutant transport are limited by the inherent lack of accessibility.

Significant accomplishments have been made in the development of methods to drill and complete wells without disturbing or altering the adjacent media to be sampled, although serious problems still exist due to the alteration of the properties of the sample during collection. The use of several geophysical techniques designed to indicate changes in groundwater quality without creating such disturbances has been researched with some success.[10,11] These techniques, however, are not yet adequate for replacing expensive monitoring wells.

Coring techniques have been developed for collecting uncontaminated samples of bacteria from the subsurface.[12] These techniques, however, are currently limited to shallow depths and certain unconsolidated geologic formations. Similar limitations face sampling techniques for most inorganic, trace organic and other biological parameters.

A major deficiency of groundwater investigations is the identification of indicator parameters for specific classes of contaminants. Limited, but promising developmental research has been completed in this area.[13]

Active research in the United States also includes evaluation of various tracer techniques, techniques for quantifying microbial populations, improvement of well completion and monitoring methods, development of methods for the prediction of the impacts

of certain mining activities on groundwater, and improvement of technology for unsaturated zone sample acquisition. Some similar efforts are underway in Europe. In addition, researchers in numerous countries have initiated work on improvement of isolation techniques for viruses in groundwater.[14]

Contaminant Transport and Fate

The development of quantitative information concerning contaminant movement and the processes of pollutant immobilization and transformation in both the saturated and unsaturated zones is the major objective of contaminant transport and fate research. Listed in increasing orders of complexity, the classes of contaminants for which this information is required are: salts, nutrients (primary), metals, organics, and bacteria and viruses.

Information on contaminant transport and fate is required to facilitate the evaluation and prediction of the effects of man's activities on groundwater quality. This encompasses the characterization of the movement of contaminants through various geologic media, including an understanding of such associated processes as sorption, chemical and biological degradation, volatilization, and fixation.

Historically, transport and fate studies have considered such inorganic contaminants as compounds of iron, nitrogen, phosphorus, and sulfur, and, to a lesser extent, metals. Of these, the least is known regarding the fate of metals and nitrogen compounds.

Knowledge concerning the transport and fate of organic contaminants in the saturated and unsaturated zones is particularly fragmentary. Until very recently, a false sense of security concerning this problem existed among most regulatory and research groups because it was inaccurately believed that a great capacity for attenuating organic compounds exists within the soil mantle. Current information concerning the presence and movement of organic compounds in the subsurface environment permits such generalized conclusions as: many organic compounds have been found to move in the groundwater environment; they undergo transformations; and, their movement is difficult to monitor. Some recent work on sediments and soils has shown natural organic matter to be of primary importance in adsorbing toxic organic chemicals moving through these materials.[15,16] Mathematical formulas capable of providing a first-generation predictive capability for a selected group of organic compounds in some subsurface environments are under development.

Because of the long-recognized health implications of pathogenic microorganisms, considerable attention has been devoted to their transport and fate in the subsurface environment.[14] Nevertheless, knowledge in this area is very limited, particularly in the case of viruses.

Groundwater quality information gathering by state agencies and universities in the United States is mainly concerned with

the transport and fate of inorganic compounds, such as nitrates and metals. In addition to the collection of data on inorganic chemicals, data on trace organic chemicals once were collected largely by the U. S. Geological Survey and through work supported by EPA. Now many organizations concerned with groundwater quality are collecting this type of information.

Even with this information gathering, deficiencies exist. A great deal of research is required in contaminant transport and fate, especially on organic and biological contaminants. Some research remains to be fulfilled with respect to metals, particularly regarding changes of oxidation-reduction states and speciation. Despite all of the work that has been accomplished with respect to nitrogen, additional and perhaps extensive efforts remain to characterize the transport and transformation of the compounds of this element in the subsurface environment. Extensive research will be required to identify classes of contaminants that have similar transport and fate characteristics and to select indicators for each of these classes. This is particularly true for organic contaminants, bacteria and viruses, and to a lesser extent for metals.

Current research efforts on organic chemicals focus on the use of simple soil columns to determine the relative mobility of selected low-molecular-weight organic compounds that are of health significance and have been implicated in groundwater contamination incidents.[17] Research on processes other than simple mobility is just beginning, and will in the future concentrate on biodegradation and sorption.

Laboratory-scale physical models (microcosms) have been constructed for study of the processes described above.[18] These models may also provide a quick screening method for judging the environmental mobility and persistence of specific chemicals of interest. They may prove particularly useful for hazardous waste identification, pesticide registration, and assessment of the environmental effects of toxic substances.

First-generation mathematical models, that utilize standard information required for registration to predict the environmental mobility of selected target pesticides, have recently become available.[19] Where field evaluation has been possible, results have been encouraging. A two-dimensional model which will ultimately be capable of using the process information from laboratory and field studies on classes of organic chemicals is under development.[20]

Studies are also under way to determine the subsurface transport and fate characteristics of viruses. Little success has been achieved to date in determining which viruses will move and survive in various environments. Work now directed toward gaining an understanding of the processes involved in transport and inactivation of viruses will likely continue for three to five years.

On the international scene, most transport studies are concerned with metals and conservative pollutants. Researchers in Sweden are looking at acid groundwater [21]; others in

the Netherlands and Switzerland are studying the subsurface transport of organic substances.[16,22,23]

Subsurface Characterization

Understanding the ecological subtleties of the subsurface environment in terms of the effect of inherent processes on pollutant transport, transformation, and fate is the basic objective of subsurface characterization efforts. Physical, chemical, and biological characteristics of the subsurface environment are identified to determine the extent to which they alter contaminant movement and composition. This information establishes the base upon which predictive models can be utilized to evaluate groundwater pollution potentials and to improve identification and predictability of changes resulting from contamination of the subsurface environment.

Researchers in such fields as agriculture, petroleum engineering, geology, geochemistry, and hydrology have developed a broad information base encompassing many aspects of the composition, structure, and hydrology of the earth. The recently recognized need for detailed information describing the interactions of pollutants with subsurface materials has accentuated the lack of attention assigned to this detail in previous research efforts.

Novel research efforts are needed to bolster the present level of available information to provide an accumulation of findings that ultimately will lead to, for example, the development of criteria for waste disposal site selection,

operation, maintenance, and closure. Initial research programs should be devoted to defining the nature of subsurface environments in terms of their innate physical, chemical, and biological characteristics leading toward the identification of key parameters that can be related to contaminant transport. Prior to this, substantial preliminary methods development research will be required, the results of which can be applied to monitoring situations. For example, a method must be developed to directly or indirectly measure the redox potential with depth.

Some research applying innovative technology to the rapid characterization of subsurface materials is developing with particular attention being given to humic-type materials [24,25] and hydrous metal oxide surfaces.[26] Other pertinent information on soil heterogeneity and property distribution has been collected in land treatment related studies here, in Europe and in Australia.[27]

THE RESEARCH STRATEGY

The processes that govern the transport and fate of pollutants in the subsurface can be divided for research purposes into three major areas: 1) hydrologic; 2) abiotic; and 3) biotic. These processes will act to influence the movement of water, the primary vehicle for subsurface pollutants, the physical and chemical interactions that will cause the pollutants to move at rates different from those of the water, and the decomposition (chemical or microbial) that will remove the pollutant from the subsurface, perhaps with the production of other equally pernicious products.

The elucidation of the importance and magnitude of the various mechanisms functioning in the three process areas will ultimately provide the knowledge that will permit the integration of the influences of these processes into a singular understanding of pollutant behavior in the subsurface.

Figure 1, a flow diagram for the groundwater research strategy, shows the inputs to the research effort and the ultimate uses of the information gained as a result. It also shows the intimate relationships among the development of a data base for groundwater pollutants, the laboratory and field research studies and the iterative process of mathematical model development. These relationships are key to addressing groundwater pollution problems now and in the future.

Current models allow crude predictions of pollutant movement on a macro-scale based primarily on information on water movement in the subsurface. Although imperfect, these models do provide a valuable function, both in the prediction of pollutant movement and in the design of research projects that address uncertainties in pollutant transport as well as in abiotic and biotic transformation. This research will in turn lead to better data for determining model coefficients and scaling down to micro-scale transport, thereby improving the resolution of the models.

The primary output of the research strategy is the development of the tools necessary for intelligent subsurface management. Management considerations include the ability to identify, evaluate,

and control potential sources of groundwater contamination, to assess impacts in emergency spill situations and to take action in restoration of groundwater quality.

Strategy Organization

Research Elements

The research strategy is fractionated into a series of concerns under each of the process areas. These concerns, or research elements, represent broad topics under which there is currently an identifiable need to provide data on subsurface pollutant behavior. The research elements are also grouped vertically according to the following parallel categories: methods development; subsurface characterization; pollutant attenuation; process kinetics--field application; and algorithm development. The nature of this structure is shown in Figures 2, 3 and 4, the hydrologic, abiotic and biotic processes, respectively.

The structure outlined in Figures 2, 3 and 4 provides a general organization of research concerns. Information gained through research in methods development and subsurface characterization will provide a basis for further research in pollutant attenuation. There is, of course, considerable overlap. This is particularly true for algorithm development, which is a continual process spanning the breadth of the research strategy.

The research elements presented in Figures 2, 3 and 4 are explained and expanded in the following sections of this chapter

under the appropriate process headings: hydrologic; abiotic; or biotic.

Hydrologic Processes. Hydrologic processes, as discussed here, include the influences of physical and chemical features of the subsurface environment on the movement of natural and/or contaminated fluids through it. These processes also include peripheral factors, such as the interaction of groundwaters with surface waters and the influences of man's activities on groundwater recharge, discharge, movement, and quality. It is necessary to thoroughly study these processes on both macroscopic, regional levels and microscopic, site-specific levels. The insights to be gained by such research are long overdue and will be costly to obtain.

Subsurface Methodology (HM1). To gain an understanding of the hydrologic processes and physiochemical features that control subsurface water movement, numerous sampling and analysis methods must be developed or further refined. These methods include: collection of subsurface rock and fluid samples by means which neither disturb nor contaminate the target sample; preservation and analysis techniques that allow for highly accurate and precise measurement of the physical and chemical properties of the sample; and, techniques (e.g., geophysical logging, remote sensing, and dynamic hydraulic testing) that rapidly and economically define variations in physical and chemical properties of the subsurface. While most of these topics have been vigorously pursued for many years, the difficulties in dealing with complex subsurface systems and the need to focus

on the movement of ultratrace contaminants have made essential even more vigorous research in this area.

Aquifer Characterization (HC1). Aquifer Characterization is a broad term denoting the thorough physical and chemical definition of an aquifer. As such, it incorporates the techniques addressed in Subsurface Methodology and further covers the use of statistical principles for efficient sampling strategies and data interpretation. Basic research regarding the fundamental geologic processes and occurrences, which led to the creation of each aquifer, is also a key component of aquifer characterization. Finally, demographic influences on aquifer behavior are required topics of study in aquifer characterization.

Pollution Plume Delineation (HC2). Methods to delineate pollution plumes include drilling followed by hydraulic testing and groundwater sampling, geophysical techniques, and physical (laboratory) simulation and computer models. Of particular importance are the dynamics of mixing/dilution processes and attenuation/retardation processes; these are currently being studied for a limited number of chemical and biological contaminants under a few of the possible field and laboratory conditions. Field efforts must continue to focus on rapid, accurate, and economical plume identification; laboratory efforts must continue to attempt to elucidate the mechanisms of plume attenuation. Major advances need be made to properly "scale up" the laboratory findings to field situations.

Spatial Variations in Hydraulic Properties (HC3). Sophisticated computer models and traditional analytical methods assume each aquifer system is homogenous or nearly so. Since this is the exception rather than the rule, methods need to be developed and/or refined to locate and accurately evaluate abrupt changes in hydraulic properties. Conventionally, methodologies have been employed to interrelate the distribution of hydraulic properties to readily measureable field parameters (e.g., static water levels). Some of these are inherently geologic, while the remainder are purely theoretical. The advances required by today's problems may be in the form of statistical approaches, geophysical techniques and remote sensing, and will come only with full integration of both geologic realities and theoretical considerations governing hydraulic properties.

Channeling (HP1). In the context used here, channeling refers to movement through fractures or other preferential avenues of fluid flow in the subsurface. These openings often exert a major control on fluid movement and, hence, on pollutant migration; they may be microscopic, such as in crystalline hard rock, or they may be quite extensive, such as in cavernous limestones and major faults. Methods are needed to locate them, map their density, and evaluate their effects on subsurface fluid flow and pollutant migration.

Macropores and Unsaturated Flow (HP2). Soil macropores commonly exert a strong accelerating influence on groundwater recharge causing relatively rapid cyclic changes in groundwater

quality, and share in the transport of microorganisms and synthetic chemicals.[7] Investigations that need to be conducted include studies of the formational processes of macropores, their physical and chemical characteristics, and the role they play in hydrologic processes.

The influence of unsaturated flow conditions on the attenuation of contaminants is as yet only poorly understood. While the fundamentally retarding impact of unsaturated conditions on fluid movement is somewhat understood, methods to predict that impact on a detailed level are underdeveloped. A great deal of the difficulty in developing satisfactory methods arises from the tremendous variability and complexity of the physical and chemical properties of unsaturated flow zones in the subsurface.

Site Specific Inhomogeneous Aquifers (HF1). Field data from investigation of aquifers with abrupt changes in thickness and hydraulic properties are the most difficult to evaluate and model with any degree of accuracy. Traditionally, information is based on drill hole data and these may be far too few to develop even a crude understanding of complex hydrologic sites. Field methods that can be used in conjunction with test hole data must be developed. Statistical analyses and innovative mapping techniques, which effectively reduce drilling and data acquisition requirements, are desperately needed.

Mathematical Description of Water Movement (HA1). Mathematical models offer the most powerful and convenient approach to prediction and management of fluid movement in the subsurface. Both analytical

and numerical mathematical models have become highly advanced in recent years. Field applications of these models have routinely lagged far behind model development, however. Field applications are greatly needed to calibrate and verify existing models. Because of the site-specific nature of the physical and chemical factors affecting fluid movement, it is still nearly impossible to create generally applicable models--much remains to be done in this area. Screening methods and benchmark problems, which can be used to assess the relative merits of various models, must be developed.

Abiotic Processes. A number of physico-chemical processes could act to attenuate the movement of pollutants in the subsurface. These processes, such as sorption and chemical reactions could serve to slow or possibly enhance movement, stimulate microbial degradation and facilitate transformation of the pollutants. An understanding of the mechanisms and extents of these processes will enable mathematical modelers to better predict the transport and fate of such chemicals in the subsurface, the potential impact of these chemicals on groundwater resources, and the probable benefits of rehabilitation efforts. The research elements enumerated under this heading focus on topics essential to advancing the knowledge of subsurface abiotic processes.

Subsurface Methodology (AM1). The collection of subsurface material and groundwater samples for monitoring or experimental purposes is crucial to developing an understanding of the behavior of pollutants in the subsurface. Additionally, methods to evaluate

treatment and rate of interactions between the pollutants and the solid phase need refinement. Recent advances in pump and well drilling technologies have enhanced the prospects of collecting minimally perturbed samples, but more development is needed, particularly with respect to volatile organic compounds and pollutants sensitive to redox conditions, approximating field conditions in laboratory interaction/reaction experiments and monitoring pollutant behavior in the field.

Identification/Characterization of Soil Constituents with Respect to Pollutant Behavior (AC1). Pollutant movement through the subsurface will be mitigated by the nature of the solid constituents and the coatings on the surfaces of these constituents. Well developed relationships for sorption of hydrophobic organic compounds to soil organic matter and for certain inorganic ions to soil mineral constituents already exist. The degree of interaction of organic and some inorganic pollutants with such soil components as clay minerals and hydrous metal oxides still remains to be defined. Research needs include: methods and quick screening tests for the measurement of the solid phase constituents; knowledge of sample storage effects and test variability; and screening techniques to determine the degree of pollutant-solid phase interactions.

Interactions and Relationships between Subsurface Constituents (AC2). Very little is known about the extent to which clays and soil organic matter and/or sesquioxides combine and how the combined material affects pollutant behavior. The

experiments that have been done to date would indicate, for example, that a chemical combination of some soil organic matter with some clays would have a much greater adsorption capacity for some pollutants than either component alone. Chemically combined compounds of clays and soil organic matter constituents are very difficult to distinguish from mixtures of these. The techniques available at the present time revolve around the use of transform infrared spectroscopy, wherein the bonds between organic matter and the mineral fraction can be determined, possibly enabling distinguishing the combined material from mixtures.

Spatial Variability of Soil Properties (AC3). Many soil properties, including organic carbon, clay content and ionic strength and composition, have been shown to influence pollutant fate in soils. Knowledge of these properties and their temporal and spatial variability is essential in accurate prediction of solute transport and in development of field scale sampling strategies. The limited efforts to date in defining spatial variability have been largely confined to generating information on hydraulic and physical properties in surface soils. Research efforts require expansion of previous efforts plus inclusion of vertical profiles of soil chemical properties.

Spatial Variations in Natural Groundwater Quality (AC4). Groundwater changes its composition along its path from recharge area to discharge zone. The details of such changes, however, both horizontally and vertically, have seldom been documented. In addition, there may be seasonal changes impressed on these

longer-term changes. Cyclic variations, often tied to critical changes of pH or Eh, have been observed in different areas of groundwater systems. Collection of in situ data on important system parameters, such as subsurface redox conditions, information critical to understanding chemical behavior of subsurface pollutants, is virtually impossible with current techniques. However, it is conceivable that common geophysical borehole techniques, such as those applied in the petroleum industry, could be applied to the measurement of subsurface environmental parameters. Information on the natural variations in groundwater quality coupled with insight into the role that such quality has on pollutant behavior will ultimately facilitate a greater understanding of pollutant mobility in the subsurface.

Relationships between Soil Constituents and Natural Groundwater Quality (AC5). A fundamental premise in groundwater geochemistry is that the composition of the groundwater is largely a result of interactions with solid materials in the subsurface through which the water passes in its path from recharge to discharge. These interactions will also greatly influence the redox potential of the groundwater. While simple inorganic chemical equilibrium reactions serve to explain and predict behavior of the high concentration salts in groundwater, methods for predicting trace level chemical changes are still awaiting development. Depending on what subsurface constituents are actively involved in solute-surface interactions, system parameters, such as pH and Eh (redox potential), will likely have a direct impact on the surface chemistry involved in such

interactions. The role of system parameters in influencing soil formation and stabilization, weathering of geologic materials and aqueous trace chemical concentrations is fundamental research requiring a much clearer definition.

Interaction of Soil Constituents and Pollutants (AP1). The interaction between pollutants, including viruses, and soil constituents is dependent on three primary factors: the nature of the pollutant; the composition of the soil; and the physical-chemical conditions of the system. The relative significance of soil components in interacting with inorganic and organic pollutants and viruses needs considerable refinement. Knowledge on the significance of system parameters, Eh, pH, soil moisture content and others, needs to be extended to the whole range of pollutants and soil components. Available information on pollutant characteristics should be focused to ascertain the relative significance of these characteristics in influencing the pollutant's behavior in the subsurface. Finally, the nature and significance of these interactions must be determined as they occur in the field.

Nature and Extent of Abiotic Reactions in the Subsurface (AP2). Subsurface environmental factors favor the occurrence of abiotic reactions, such as hydrolysis and redox reactions, in addition to, or possibly in conjunction with, microbial activity. Three factors in particular would function to enhance abiotic reactions: these are large surface areas of clays and metal oxides, reactive moieties in soil and dissolved organic matter, and the slow movement of groundwater providing long contact times. Laboratory methodologies

for reproducing the conditions necessary to investigate the nature and extent of such reactions and the environmental conditions that influence them remain to be devised, and field capabilities in this area are currently quite limited. Additionally, the interrelationships between surface, abiotic and biotic reactions in the subsurface will need to be defined before the degradative processes can be understood.

Effects of Large Amounts of Pollutants (AP3). Large amounts of pollutants can be introduced into the subsurface as a result of accidental spills, breaches in waste disposal pond or landfill integrity or unlawful disposal practices. Movement of large amounts of pollutants through the subsurface will likely produce disruptions in natural biotic and abiotic processes and changes in physical-chemical subsurface characteristics. For example, the potential for clay alterations by organic solvents has been demonstrated.[28] While numerous examples of the introduction of large amounts of pollutants into the subsurface are cited in the literature, very little research has focused on the effects from such occurrences or the development of information to minimize the consequences.

Extent of Dispersion and Diffusion (AP4). The dispersion term that appears in most solute transport equations, which describes the distribution or shape of a noninteracting chemical front or pulse moving through porous media, represents a combination of molecular diffusion and hydrodynamic dispersion. In practice, however, this term is often used as a "catchall" for other poorly

understood or defined processes. Field measurement of dispersion is an extremely difficult task. Future research needs to focus on the relationships of dispersion to the characteristics of the fluid, the porous media and the environmental system and on the relative significance of dispersion and other transport properties, i.e., adsorption, mass flow, and degradation, especially for trace level pollutants.

Extent and Rate of Volatilization from the Subsurface (AK1). It is likely that volatilization from the saturated and unsaturated zones accounts for a major fraction of trace organic losses from the subsurface. Volatilization kinetics of organic compounds from water in a beaker are reasonably well-defined, but the extension of this information to subsurface systems has not been well-documented. Field studies with relatively nonvolatile pesticides have shown that soil characteristics influence volatility. Clearly, the theory of volatilization from partially water-saturated soils needs development. Field methods development followed by field studies on trace organics will provide information essential to optimizing both the theory and the predictive basis of volatilization.

Extent and Rate of Soil Attenuation of Pollutants (AK2). A predictive understanding of the abiotic processes that influence pollutant movement in the subsurface necessitates knowledge of the kinetics and the magnitude of these processes. Current knowledge in this area is limited to certain inorganic ions on surface soils and to hydrophobic organic pollutants in relatively high organic carbon soils, those systems where the interactions

are of the greatest magnitude and are most easily defined. Future research will expand to cover the range of pollutant types and the variety of subsurface systems encountered in the environment. The ultimate measure of this research will be its ability to provide, directly or through extrapolation, the information needed to evaluate any pollutant transport problem encountered in the subsurface.

Mathematical Description of Mass Transport Properties (AA1). Mathematical description of mass transport properties of subsurface systems are essential to the proper design and execution of the research efforts outlined in this strategy and, ultimately, to the accurate prediction of pollutant movement in the subsurface. Such models currently represent an integration of several poorly defined topical areas including numerous hydrologic and chemical relationships that still require extensive research to develop them to a functional level of understanding. The modelling process, however, will be one of continual refinement, with the accuracy of model predictions, and hence, their utility, improving as these subsurface relationships become better defined.

Biotic Processes. The extent and nature of microbial activity in the subsurface must be understood to more effectively develop groundwater quality management practices. Just as microorganisms are by far the most important agents that transform organic compounds in surface soils and waters, an active subsurface biota could have a profound effect on the movement and persistence of

pollutants in subsurface materials and waters. On the other hand, the absence of appreciable microbial activity in subsurface regions will signify that the fate of pollutants in groundwater will be controlled by abiotic processes only. The research elements discussed in the Biotic Processes category delineate key research topics for developing necessary information on subsurface biotic processes in order to predict the transport, fate, and impact of pollutants in the subsurface and to develop control and remedial technology for groundwater quality.

Subsurface Methodology (BM1). The major deterrent in the study of subsurface biological processes is a lack of reliable and/or inexpensive methods for examining the subsurface. Considerable progress has been made in recent years in developing methods for obtaining uncontaminated samples, in developing new techniques and procedures for characterizing subsurface biota, and in developing technology for determining how biological processes affect pollutant transport and fate. However, improvement is needed in all of these areas. Currently coring procedures are slow, cumbersome, expensive, and only work in certain types of subsurface materials. Whether cores should be handled under anaerobic conditions is not definitely known. The proper procedures for sampling well microflora have not been established, nor has it been determined what the value of such samples is. Methods for measuring in situ activity and conditions affecting that activity have been primarily limited to the use of physical models that are in the first stages of development and evaluation. Techniques

and procedures for determining biomass, measuring important environmental conditions, such as redox potential, examining ecological interactions, and determining the specific metabolic activities and capabilities of subsurface microflora, are in the developmental stages and need continued improvement.

Nature and Vertical Extent of Subsurface Biota (BC1). The presence or absence of a subsurface biota could have a profound effect on the persistence of certain pollutants in groundwater. In regions of the subsurface that lack microbes in sufficient densities, the transport and fate of many pollutants will be controlled by abiotic processes and will, therefore, be easier to predict. Current information indicates that the deeper subsurface environment is not sterile and that there may be considerable spatial variation in microbial populations both from a qualitative and quantitative standpoint. These conclusions, however, are based on a very limited number of studies and far more information on the distribution, density, and nature of organisms in the subsurface, both above and below the water table, is needed. Further studies should emphasize correlating the occurrence and activities of organisms with the geological and mineralogical properties and the environmental conditions of the subsurface regions where the organisms exist.

Effect of Interactions Between Subsurface Organisms (BC2). A divergent microflora is known to occur in at least some regions of the subsurface and may have a significant impact on the fate

of many groundwater pollutants. Almost nothing is known of the interactions of subsurface organisms with each other or with surface organisms that enter that environment. In surface habitats such interactions can be extremely important in determining the fate of chemical or biological pollutants. For example, a microbial species with the ability to degrade a particular compound may not be able to compete for required nutrients with other organisms. Some microbes are dependent upon the byproducts of other microbes' metabolisms. Whether such interactions are important in determining the fate of groundwater pollutants is unknown.

Nature and Extent of Biotic Reactions in the Subsurface (BP1). At present little is known about biodegradation of organic pollutants in the deeper subsurface. Current knowledge indicates that the microflora of shallow regions of the saturated zone can degrade certain organic pollutants, but cannot degrade others that are easily degraded in surface soil.[17] Additionally, microbes from different sites vary in their ability to degrade particular organic pollutants.

A limited amount of pollutant biodegradation research has been done using the autochthonous flora of the subsurface and foreign pollutants; virtually no work has been accomplished in situ. These results have indicated that the potential for significant biodegradation of a number of compounds exists. However, the question remains unanswered as to the degree to which these reactions will proceed in the subsurface. The limitations have not been clearly defined to be either thermodynamic

(energy-limited) or kinetic (rate-limited) nor has the extent of adaptation and cometabolism been investigated in detail. Very little is known concerning degradation byproducts or whether degradation processes can be manipulated.

Effect of Pollutants on Microflora (BP2). Little effort has been expended to determine what effect pollutants have on indigenous subsurface microflora. Such effects may be environmentally undesirable. For example, recent studies on the fate of pollutants in high rate land treatment systems shows that certain metals and organic compounds temporarily stopped nitrification.[29,30] It is very possible that certain pollutants will be toxic to subsurface microbes and stop them from degrading pollutants that are not toxic to the same microbes. Another consideration is the mutagenicity of introduced pollutants, both to indigenous microflora and to introduced organisms, especially pathogens.

Effect of Geochemical Parameters on Biological Activity (BP3). The subsurface environment differs considerably from normally studied microbiological habitats found in surface waters or soils. Little is known concerning environmental conditions in subsurface habitats and the effect such conditions have on biological activity and the biotic transformation of pollutants. Important factors governing the extent and/or nature of biological activity include: 1) the concentration and utility of electron acceptors; 2) the concentration and availability of essential nutrients; 3) the oxidation-reduction potential; 4) the pH; 5) the ionic composition; 6) the availability of water; 7) the

temperature; 8) the hydrostatic pressure; 9) the nature of the solid phase; and 10) the nature of the pore space. All of the above factors interact with each other to influence the activity of organisms in the subsurface.

Rates of Biological Transformations (BK1). Biodegradability and the associated kinetic relationships should be determined prior to development and use of mathematical models for predicting the movement and fate of pollutants in the subsurface environment. Volatilization and sorption should be determined to predict biodegradation, since a mass balance is required. Reaction kinetics should be determined for modeling. Studies are required to determine: 1) the effect of concentration of pollutant on the rate law for transformation; 2) the effect of concentration of pollutant on the density of microbes active against that pollutant; and 3) the correlation between the rate of transformation of the pollutant and the density of viable microbes, or the concentration of some biochemical constituent of the microbes used as an indicator of biomass or nutritional state. Current information is scant. Mathematical modelers tend to assume that biotransformations are first order. Detailed studies of biotransformation kinetics in material from the deeper subsurface are almost nonexistent, however, work on NTA [31] and on chlorobenzene and dibromochloromethane [12] suggest zero-order kinetics, at least at concentrations of 1-30 mg/l.

Mathematical Description of Biotic Kinetic Processes (BA1). To use laboratory and field information about subsurface biotic reactions to predict the fate of pollutants requires the development of mathematical submodels that describe the kinetics of biological transformations in the subsurface, and which can be incorporated into more sophisticated mass transport models describing water movement and abiotic attenuation of pollutants. Successful development of a viable biotic processes submodel will be dependent upon the determination of biotransformation kinetic information. Current mass transport models are deficient in handling biotic processes.

SUMMARY

The importance of protecting groundwater resources cannot be overstated, and many people throughout the world seem anxious to physically and financially support a rational program to this end. The complacency of the public regarding the quality of groundwater was destroyed with headline-grabbing incidences of pollution such as Love Canal. Contrary to earlier popular belief, the soil mantle has been shown to be ineffective in the cleansing of certain pollutants from the water flowing through it.

The legislative basis for developing and implementing a groundwater quality management scheme exists, although it is dispersed in a variety of pieces of legislation. Such a management scheme presupposes the existence of the scientific knowledge necessary to produce viable and effective results from its implementation. This chapter has addressed the research

needs for accumulation of this scientific knowledge.

The Ground Water Research Branch, Robert S. Kerr Environmental Research Laboratory, EPA, Ada, Oklahoma, has been given the task of expanding knowledge of pollutant transport and fate in the subsurface to the point where effective action can be taken to prevent or limit groundwater pollution and rehabilitate already existing contaminated systems within the context of an overall groundwater management scheme. The dearth of knowledge that stems from previous disinterest of the public to groundwater pollution problems makes this task arduous and expensive. This document describes an organized and coordinated approach to this task.

Groundwater research strategy considerations are divided into three areas based on the types of processes that will affect pollutant movement in the subsurface: 1) hydrologic; 2) abiotic; and 3) biotic processes. Research under each of these process areas is further organized into a skeleton of research elements focusing on methods development, subsurface characterization, pollutant attenuation, process kinetics, field application and mathematical model development and application. Each of these research elements represents a series of tasks or specific questions that need to be addressed.

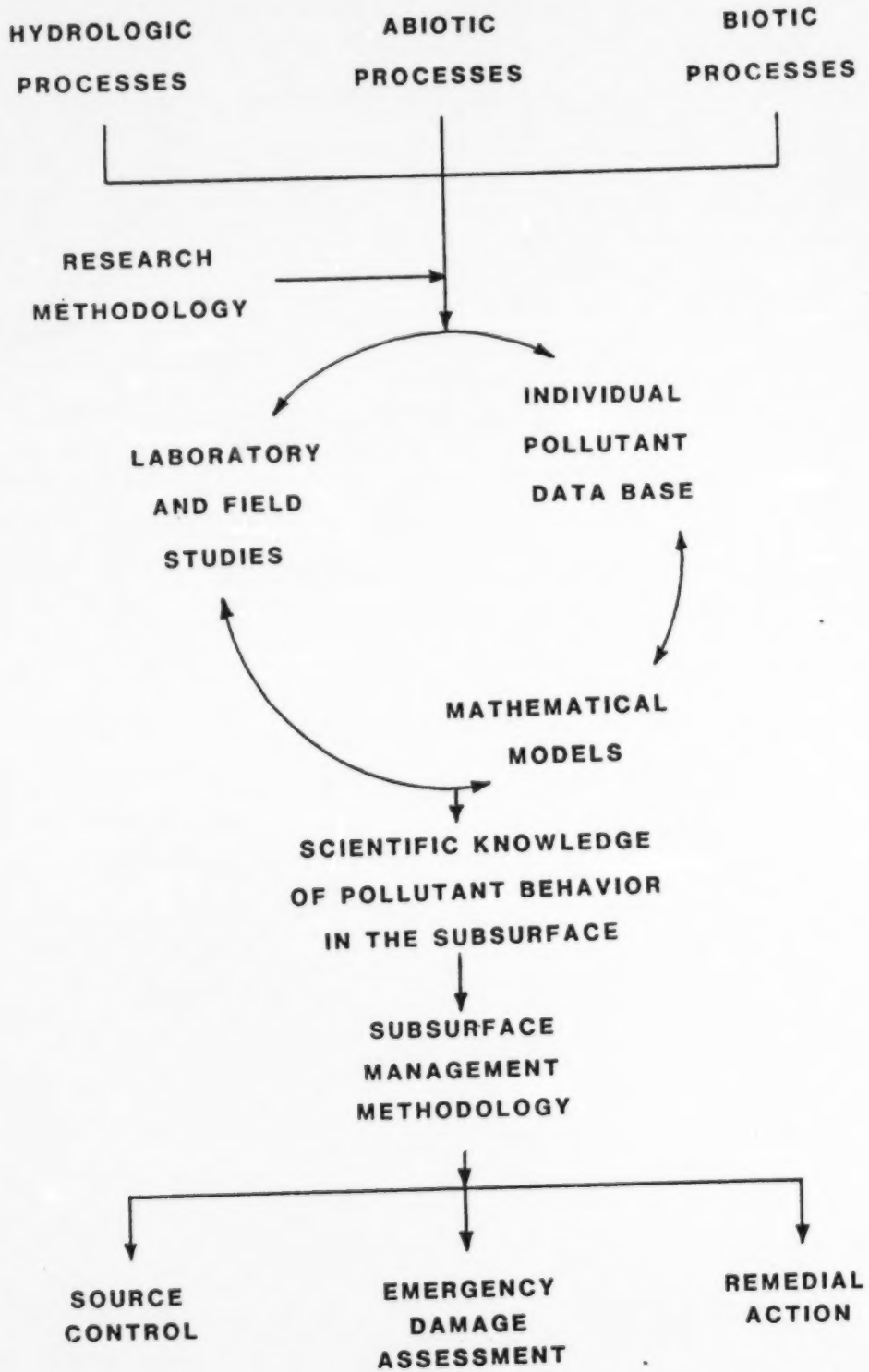
The research elements are intended to serve as a first-level planning base for use by groundwater research planners. The elements facilitate the orderly development of a series of specific research topics, or tasks, which need to be addressed to expand

the existing knowledge of pollutant subsurface behavior. It is at the task level that the inherent flexibility of this becomes apparent. The addition of tasks under the various research elements will be a somewhat continuous process, at least through the early years of a research program. The research element outline will provide a skeleton for organization and direction of these tasks.

Attempts to compartmentalize environmental processes are doomed to failure unless constant attention is paid to the interactions of the compartments as they occur in the natural systems. The research outlined in the foregoing has been divided into three compartments to permit researchers to focus on the nature and extent of the processes that affect pollutant transport. The authors are keenly aware of the likelihood that these processes are intimately related in the actual subsurface. As the knowledge of subsurface processes begins to grow, the nature of these interactions will become more obvious and the research required to determine their significance will become more easily defined.

The purpose here is to provide an organized approach to planning both short- and long-term groundwater quality research. It should be available to government personnel charged with matching budgeted funds to priority research areas and to research people responsible for the conception, design and conduct of groundwater research. Following this evolving outline, the regulatory and research groups can proceed in an orderly fashion toward solving the problems posed by groundwater contamination.

GROUND-WATER RESEARCH STRATEGY



HYDROLOGIC PROCESSES

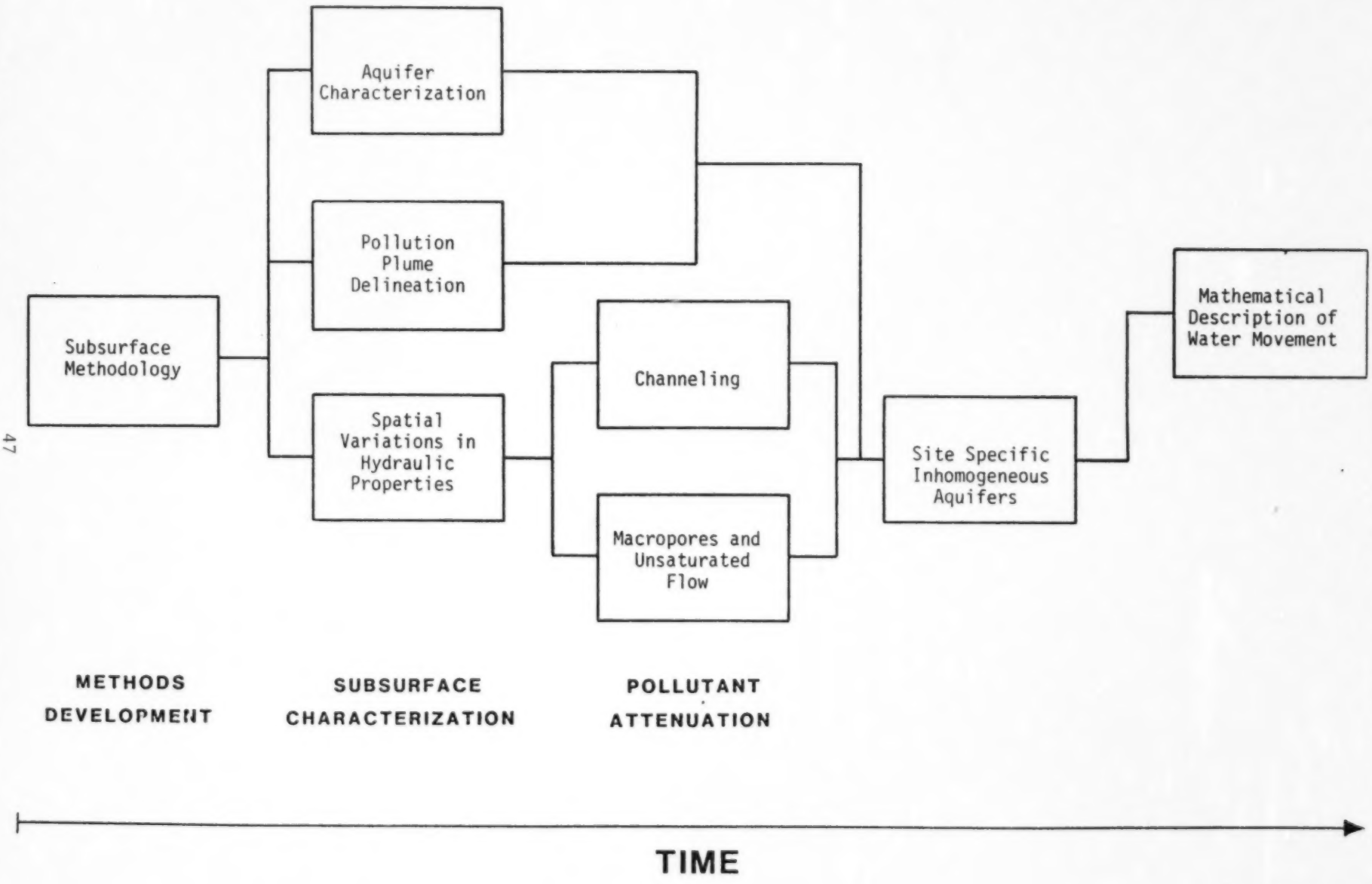
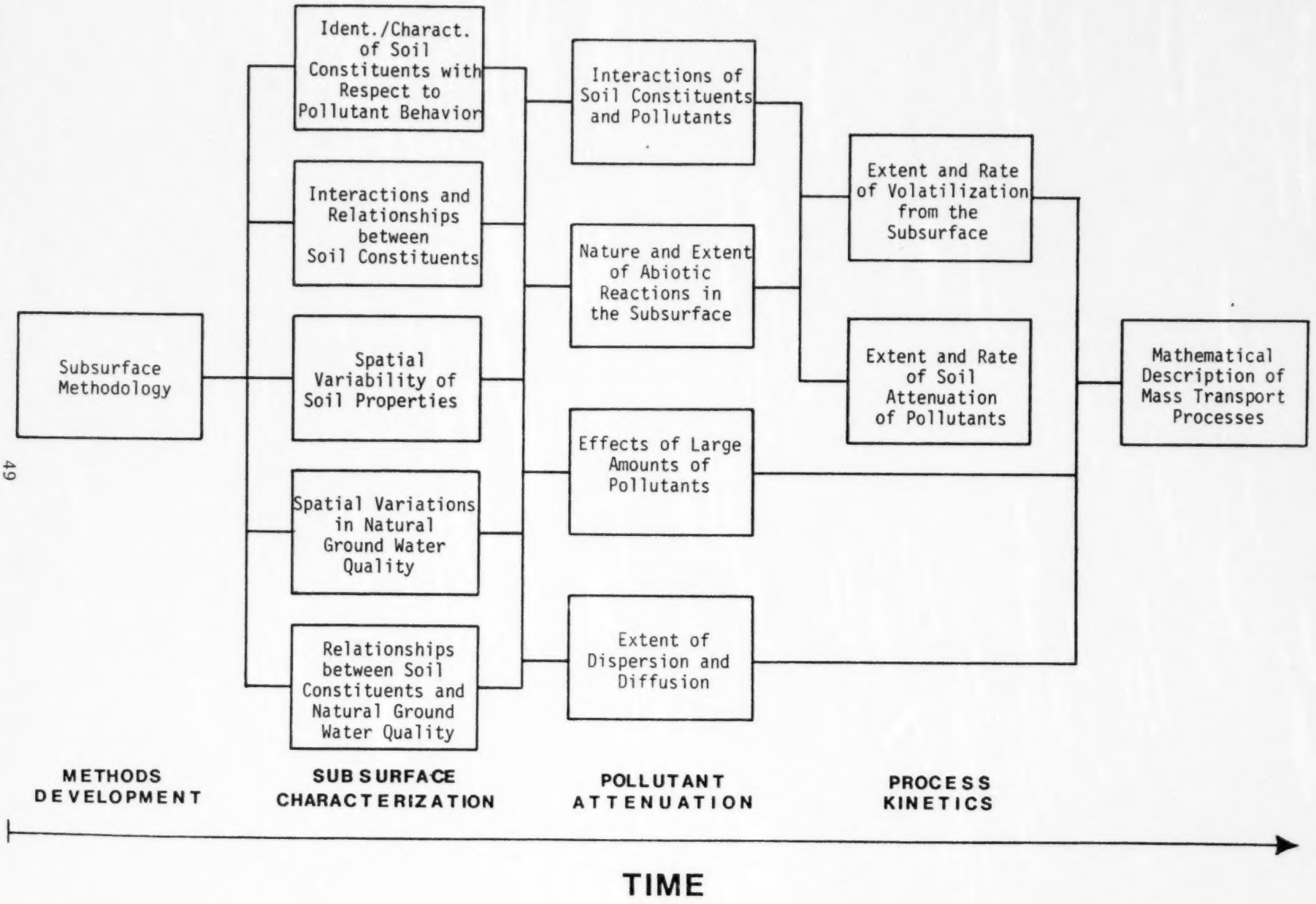


Figure 2. Hydrologic Processes.

ABIOTIC PROCESSES


Subsurface Methodology
Ident./Charact. of Soil Constituents with Respect to Pollutant Behavior
Interactions and Relationships between Soil Constituents
Spatial Variability of Soil Properties
Spatial Variations in Natural Ground Water Quality
Relationships between Soil Constituents and Natural Ground Water Quality
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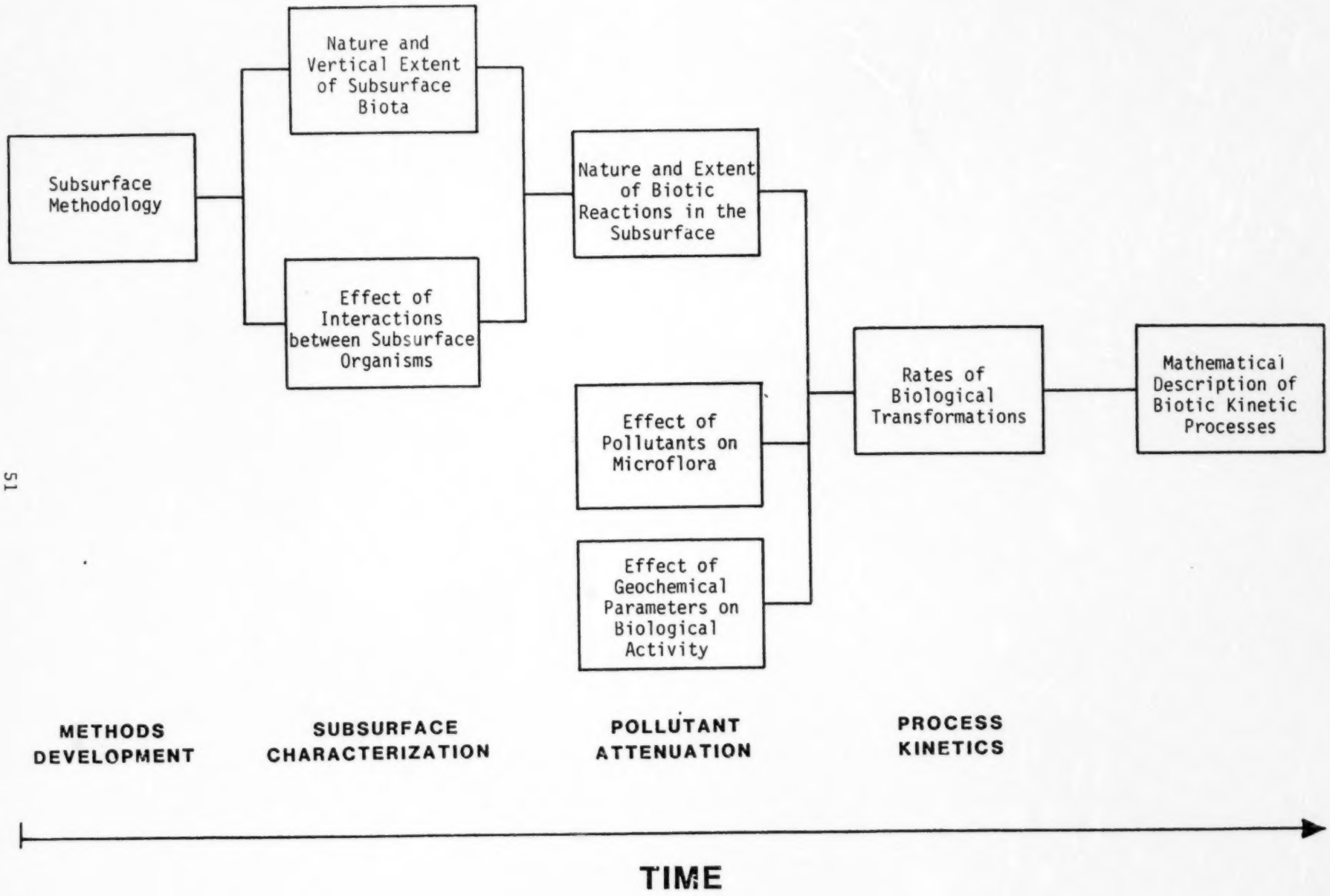
Extent and Rate of Soil Attenuation of Pollutants
Mathematical Description of Mass Transport Processes
METHODS DEVELOPMENT
SUB SURFACE CHARACTERIZATION
POLLUTANT ATTENUATION
PROCESS KINETICS
TIME

Figure 3. Abiotic Processes.

BIOTIC PROCESSES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PROCESS KINETICS
TIME

Figure 4. Biotic Processes.

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